



Determination of ultratrace elements in semiconductor grade Isopropyl Alcohol using the Thermo Scientific iCAP TQs ICP-MS

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Keywords

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Goal

To determine ultratrace metal concentrations in semiconductor grade isopropyl alcohol (IPA). Use cold plasma and triple quadrupole technologies to reduce background equivalent concentrations (BEC) and detection limits (LOD). Demonstrate the use of the Thermo Scientific™ iCAP™ TQs ICP-MS to perform reproducible ultratrace $\text{ng}\cdot\text{L}^{-1}$ (ppt) measurements with reliable switching between multiple analysis modes (hot/cold plasma, single/triple quadrupole) within a single measurement.

Introduction

Isopropyl alcohol (IPA) is used to clean wafers during production in the semiconductor industry. As IPA comes into direct contact with wafer surfaces, it must be controlled for its trace metal purity. Because of its high elemental sensitivity, ICP-MS is widely used in quality control analyses of materials in the semiconductor industry. An ICP-MS technique for the direct analysis of IPA would provide a useful control for ultratrace ($\text{ng}\cdot\text{L}^{-1}$) levels of analytes in IPA and avoid any contamination caused by sample preparation.

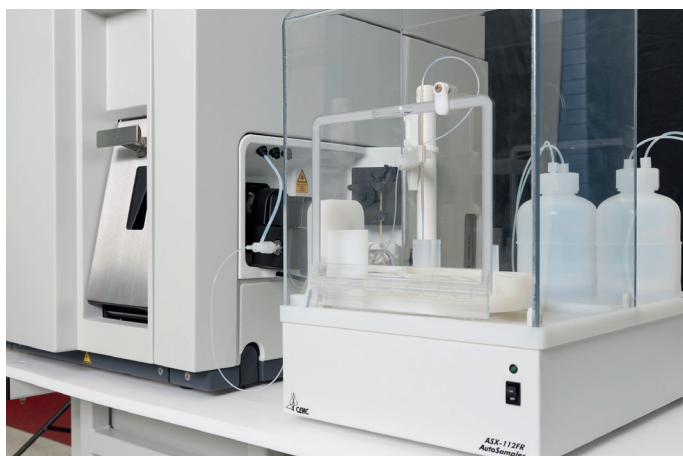
IPA has historically been considered a difficult matrix to analyze directly by ICP-MS due to its high volatility, low viscosity and high carbon content.

In this application note, cold plasma and triple quadrupole ICP-MS technologies are combined within a single analytical method to remove sample matrix and argon based interferences. With the use of cold plasma, the ICP ion source is run at a significantly lower power, effectively suppressing the ionization of argon and carbon and therefore eliminating polyatomic species that would otherwise interfere with target analyte ions. For some analytes that are more sensitive in hot plasma, a triple quadrupole mass shift analysis mode was employed for accurate, interference free analysis.

The highly flexible approach offered by the combination of triple quadrupole and cold plasma technologies in the Thermo Scientific™ iCAP™ TQs ICP-MS achieves the ultratrace background equivalent concentrations (BEC) and detection limits (LOD) required by the semiconductor industry.

Sample preparation

Pre-cleaned PFA bottles were used for the preparation of all blanks, standards and samples. The bottles were rinsed with ultrapure water (18.2 MΩ) and left to dry in a laminar flow clean hood before use. Standards at concentrations of 15.7, 39.3, 78.6 and 157.2 ng·L⁻¹ (with the exception of phosphorous which was ten times higher) were prepared by gravimetrically adding the appropriate quantity of a multielemental stock solution (prepared from single element standards) directly to the IPA samples. Semiconductor grade IPA was used for the rinse and blank solutions.



Instrumentation

A dedicated organic matrix sample introduction system was used for the routine, direct analysis of IPA. The introduction system consisted of a 100 μL·min⁻¹ self-aspirating PFA micro flow concentric nebulizer (Elemental Scientific, Omaha, NE, USA) and a peltier cooled quartz spraychamber (at -10 °C). High purity oxygen was added to the aerosol stream via a port in the spraychamber elbow to prevent carbon matrix build up on the interface. A 1.0 mm diameter quartz injector minimized carbon loading of the plasma. Platinum tipped sampler and skimmer cones were necessary because of the oxygen addition. All samples were presented for analysis using a Teledyne CETAC Autosampler ASX-112FR System (Omaha, NE, USA).

The iCAP TQs ICP-MS was operated in triple quadrupole modes (TQ-O₂ mass shift and TQ-NH₃ mass shift mode) and single quadrupole modes (Hot, KED and Cold) using the parameters presented in Table 1. The iCAP TQs ICP-MS used in this study was not installed in a cleanroom.



Table 1. Instrument configuration and operating parameters.

Parameter	Value					
Nebulizer	PFA concentric Nebulizer 100 μL·min ⁻¹ (self-aspirating)					
Spraychamber	Quartz cyclonic spraychamber cooled at -10 °C					
Injector	1.0 mm I.D., Quartz					
Interface	Pt sampler and Pt skimmer					
Extraction lens	Cold plasma lens					
Measurement Mode	Single quadrupole modes				Triple quadrupole modes	
	SQ-STD	SQ-KED	SQ-CP	SQ-CP-NH ₃	TQ-O ₂	TQ-NH ₃
Forward Power	1450 W		600 W		1450 W	
Additional Gas	Pure O ₂ gas 30 mL·min ⁻¹					
Nebulizer Gas	0.60 mL·min ⁻¹	0.60 mL·min ⁻¹	0.85 mL·min ⁻¹	0.85 mL·min ⁻¹	0.60 mL·min ⁻¹	0.60 mL·min ⁻¹
CRC Gas	-	Pure He 4.2 mL·min ⁻¹	-	Pure NH ₃ 0.28 mL·min ⁻¹	Pure O ₂ 0.3 mL·min ⁻¹	Pure NH ₃ 0.28 mL·min ⁻¹
Dwell Time	100 to 300 ms per analyte, 5 sweeps					
Lens Setting	Optimized via autotune procedure					

Figure 1 demonstrates plasma properties with and without oxygen whilst running IPA. All iCAP Qnova Series ICP-MS instruments include a high resolution video camera inside the torch box for direct observation of the plasma, useful for method development or diagnostic purposes. Without oxygen addition, an intense emission of green light at the cone surface is observed and carbon will deposit on the cone, leading to clogging and soon after a decrease of the attainable signal intensity. Optimized oxygen addition shows a complete elimination of the carbon based emission leading to improved signal stability. Further increase of the oxygen flow will not lead to a significant increase in performance.

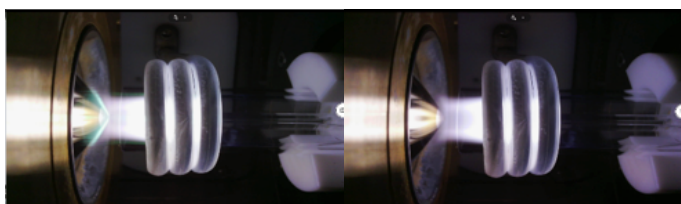


Figure 1. Plasma properties during IPA analysis without and with oxygen gas addition (left: without oxygen, right: with oxygen).

Cold plasma – analysis with a forward power of 600 W – was used to inhibit the formation of argon and carbon based polyatomic interferences and reduce backgrounds of low ionization potential (IP) elements such as Li, Na and K. Figure 2 demonstrates plasma properties in hot and cold plasma operation.

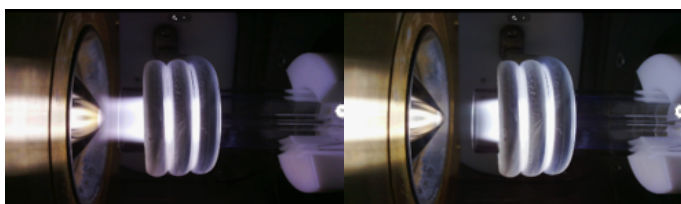


Figure 2. The plasma condition of hot and cold plasma (Left: hot plasma, Right: cold plasma).

All instrument parameters in each of the measurement modes were defined automatically using autotune procedures provided in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software. The autotune functionality ensures that plasma and interface related settings, such as nebulizer flow and extraction lens voltage, are automatically applied across all associated measurement modes so that the sample is processed in exactly the same way in the plasma, independent of the collision/reaction cell (CRC) and quadrupole settings. Details about the settings used for the different modes are shown in Table 1.

Results and discussion

The Thermo Scientific iCAP TQs ICP-MS system is a powerful analytical tool for the multielemental analysis of high purity chemicals. By providing the analyst with the complete range of ICP-MS technologies (cold plasma, kinetic energy discrimination and triple quadrupole), the ultimate performance can be achieved, specifically tailored for each application. Through the implementation of Reaction Finder in the Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, the choice of isotope and analysis mode for each target element is made automatically, making triple quadrupole ICP-MS as easy to use as single quadrupole systems.

For example, using the TQ-O₂ mass shift mode (schematically shown in Figure 3) polyatomic interferences are efficiently removed at ³¹P, providing ultratrace BEC and LOD detection capabilities. In TQ-O₂ mass shift mode, the first quadrupole (Q1) uses Intelligent Mass Selection (IMS) to transfer ions of a specific mass into the CRC eliminating ions that could potentially lead to new interferences. The second quadrupole (Q2) is then used to selectively shift the ³¹P target analyte (using O₂ as the reaction gas) to the ⁴⁷[PO]⁺ product ion, while any remaining carbon based polyatomic interference will not react with O₂. The third quadrupole (Q3) then isolates the target product ion ⁴⁷[PO]⁺, removing any residual interferences through a second stage of mass filtration allowing for completely interference free quantification.

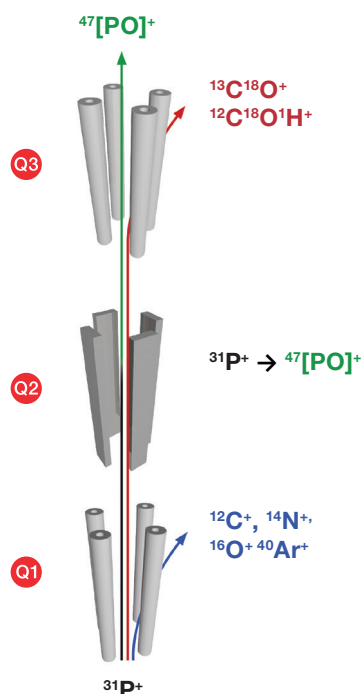


Figure 3. Schematic showing TQ-O₂ mass shift mode for the analysis of ³¹P as ⁴⁷[PO]⁺.

As can be seen in Table 2, BEC and LOD values (calculated from three times the standard deviation of ten replicate measurements of the calibration blank) were determined for 35 elements in IPA.

Table 2. BEC, LOD and recovery data for the analysis of semiconductor grade IPA. Please note that BEC and LOD values are dependent on the sample provided for analysis and do not necessarily demonstrate the ultimate performance possible.

	Analysis Mode	BEC (ng·L ⁻¹)	LOD (ng·L ⁻¹)
⁷ Li	SQ-CP	0.1	0.01
⁹ Be	SQ-STD	0.7	0.2
²³ Na	SQ-CP-NH ₃	3.3	0.4
²⁴ Mg	SQ-CP-NH ₃	0.6	0.3
²⁷ Al	SQ-CP-NH ₃	13.9	0.6
³¹ P at m/z 47	TQ-O ₂	1069	99
³⁹ K	SQ-CP-NH ₃	1.4	0.5
⁴⁰ Ca	SQ-CP-NH ₃	6.0	1.1
⁴⁸ Ti at m/z 114	TQ-NH ₃	0.2	0.001
⁵¹ V at m/z 67	TQ-O ₂	2.0	0.4
⁵² Cr	SQ-CP	4.7	0.9
⁵⁵ Mn	SQ-CP-NH ₃	0.4	0.1
⁵⁶ Fe	SQ-CP-NH ₃	5.0	0.8
⁵⁹ Co	SQ-CP	0.2	0.1
⁶⁵ Cu	SQ-CP	7.6	0.6
⁶⁶ Zn	SQ-CP	1.0	0.4
⁷¹ Ga	SQ-CP	0.07	0.1
⁷⁴ Ge	SQ-KED	3.0	0.6

	Analysis Mode	BEC (ng·L ⁻¹)	LOD (ng·L ⁻¹)
⁷⁵ As at m/z 91	TQ-O ₂	4.0	0.9
⁸⁰ Se at m/z 96	TQ-O ₂	0.7	1.3
⁸⁵ Rb	SQ-CP-NH ₃	0.2	0.1
⁸⁸ Sr	SQ-CP	0.04	0.07
⁹⁰ Zr	SQ-KED	0.03	0.04
⁹⁵ Mo	SQ-STD	0.6	0.2
¹⁰⁷ Ag	SQ-STD	0.1	0.08
¹¹¹ Cd	SQ-STD	0.001	0.001
¹¹⁵ In	SQ-STD	0.2	0.04
¹¹⁸ Sn	SQ-STD	5.4	1.2
¹²¹ Sb	SQ-STD	0.05	0.01
¹³⁸ Ba	SQ-KED	0.01	0.04
¹⁸¹ Ta	SQ-STD	0.1	0.04
¹⁹⁷ Au	SQ-STD	0.3	0.09
²⁰⁵ Tl	SQ-STD	0.01	0.04
²⁰⁸ Pb	SQ-CP-NH ₃	0.2	0.3
²⁰⁹ Bi	SQ-STD	0.06	0.02

Calibration data

Calibration curves for Li, P, K, Ti, As, Zr and Ta in IPA, are shown in Figure 4. The calibrations, performed with calibration standards in the ng·L⁻¹ (µg·L⁻¹ for P) range, showed excellent linearity and sensitivity. The low backgrounds achieved for the more challenging analytes was possible through improved interference removal with triple quadrupole modes and cold plasma operation.

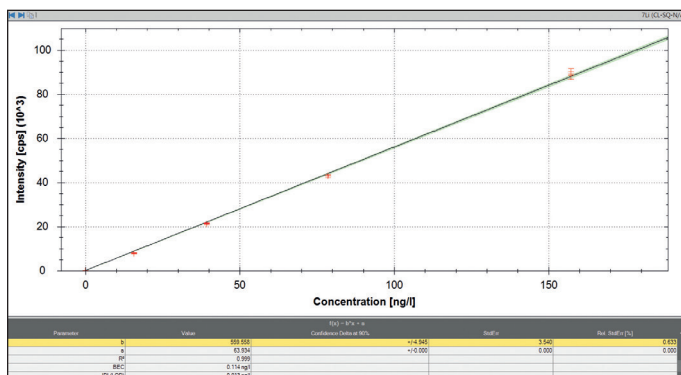


Figure 4a. Li in SQ-CP mode.

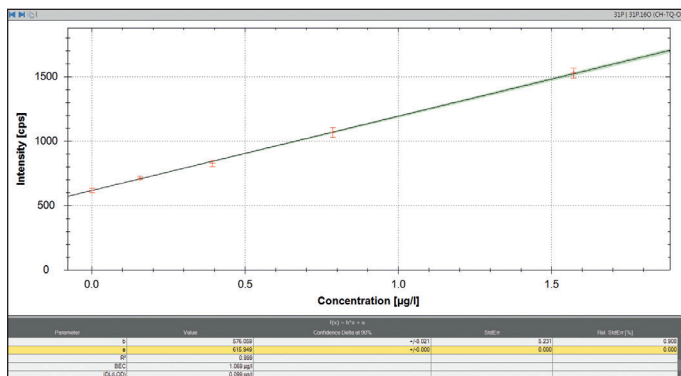


Figure 4b. P in TQ-O₂ mass shift mode.

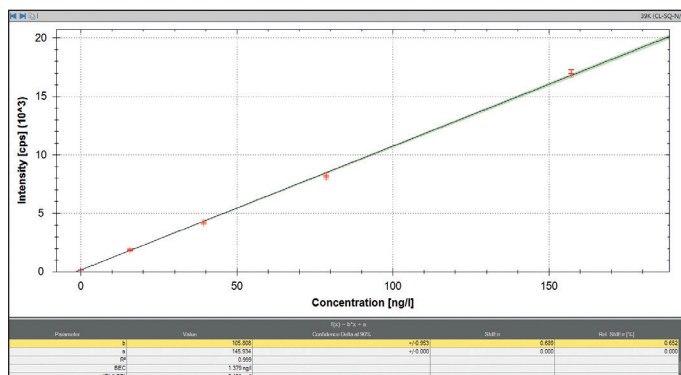


Figure 4c. K in SQ-CP-NH₃ mode.

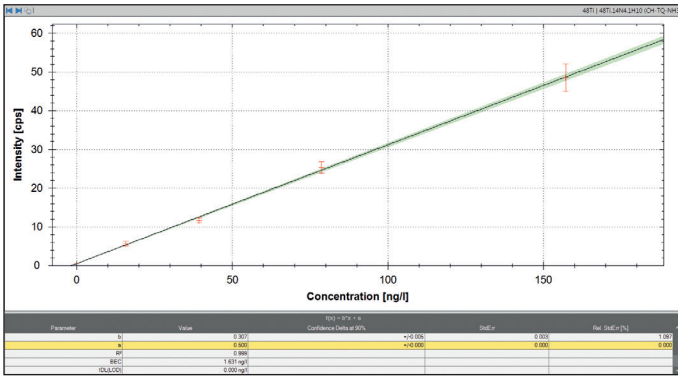


Figure 4d. Ti in TQ-NH₃ mass shift mode.

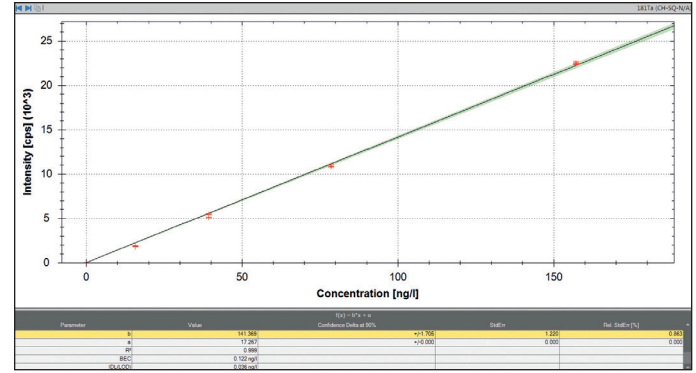


Figure 4g. Ta in SQ-STD mode.

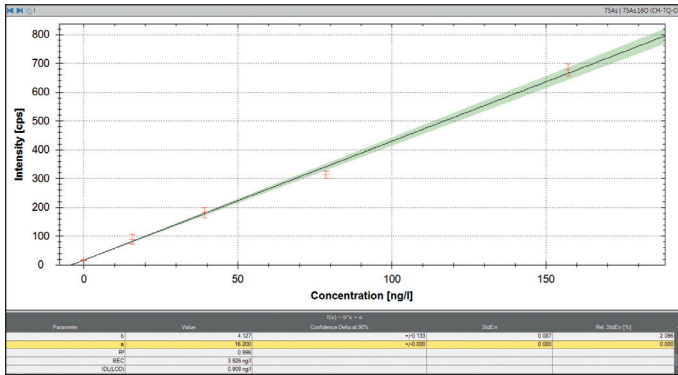


Figure 4e. As in TQ-O₂ mass shift mode.

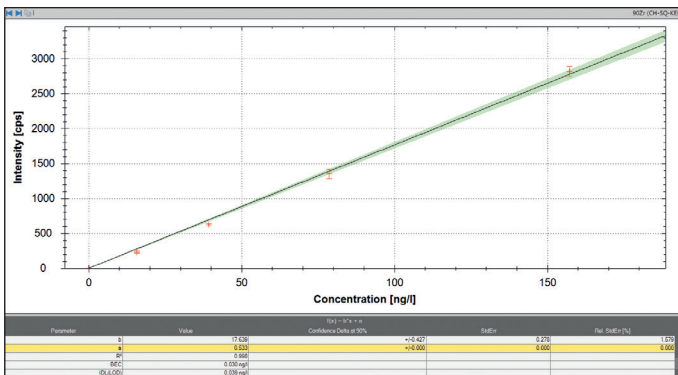


Figure 4f. Zr in SQ-KED mode.

Figure 4. Calibration curves in IPA.

Conclusion

The Thermo Scientific iCAP TQs ICP-MS has been shown to provide the sensitive and accurate multielemental analysis of semiconductor grade IPA at ultratrace (ng·L⁻¹) concentration levels. The combination of single and triple quadrupole technologies with or without cold plasma delivers the flexibility to deliver optimum conditions for all analytes to reduce background equivalent concentrations and achieve excellent detection limits.

The reliable switching between multiple analysis modes on the iCAP TQs ICP-MS enables smooth transitions between hot and cold plasma modes and single or triple quadrupole modes within a single measurement, improving ease of use and productivity.

Find out more at thermofisher.com/TQ-ICP-MS

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